

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C03C 3/087, 3/093</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/19559</b> <b>(43) International Publication Date:</b> 12 November 1992 (12.11.92)
<b>(21) International Application Number:</b> PCT/CS92/00012 <b>(22) International Filing Date:</b> 6 May 1992 (06.05.92) <b>(30) Priority data:</b> 1344 - 91 8 May 1991 (08.05.91) CS <b>(71) Applicant (for all designated States except US):</b> VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ ÚSTAV SKLA A KERAMIKY [CS/CS]; Technická 5, 166 28 Prague (CS). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> ŠAŠEK, Ladislav [CS/CS]; U Petřín 1858/6, 162 00 Prague 6 (CS). RADA, Miroslav [CS/CS]; Americká 247, 345 61 Staňkov (CS). ŠAŠEK, Ladislav [CS/CS]; Mečíkova 2835/2, 106 00 Prague 10 (CS).		<b>(74) Agent:</b> SMRČKOVA, Marie; Na bojišti 12, 120 00 Prague 2 (CS). <b>(81) Designated States:</b> AT (European patent), BE (European patent), BG, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), RU, SE (European patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LEAD-FREE CRYSTAL GLASS  <b>(57) Abstract</b> <p>Crystal lead-free glass suitable for man-made and machine-made utility glass especially of luxurious character with a higher refractive index, containing in % by weight from 50 to 65 of silicon dioxide SiO<sub>2</sub>, from 0.1 to 10 of aluminium oxide Al<sub>2</sub>O<sub>3</sub>, from 0.5 to 17 of zirconium dioxide ZrO<sub>2</sub>, from 10 to 22 of potassium K<sub>2</sub>O and/or sodium Na<sub>2</sub>O oxide, from 2 to 10 of calcium CaO and/or magnesium MgO oxide, the content of ferric oxide Fe<sub>2</sub>O<sub>3</sub> being within the range from 0.01 to 0.025 % by weight. The properties of said glass are modified at least by one oxide from the group comprising barium BaO, zinc ZnO, boron B<sub>2</sub>O<sub>3</sub> and lithium Li<sub>2</sub>O oxides. The further modifiers are either individually or in combination antimony trioxide Sb<sub>2</sub>O<sub>3</sub>, titanium dioxide TiO<sub>2</sub> and stannic dioxide SnO<sub>2</sub> within the range from a trace to 1 % by weight of antimony trioxide Sb<sub>2</sub>O<sub>3</sub>, titanium dioxide TiO<sub>2</sub> and stannic dioxide SnO<sub>2</sub>.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

- 1 -

## Lead-free crystal glass

### Technical field

5        This invention relates to crystal lead-free glass which is intended especially for the man-made and machine-made utility glassware, with the refractive index within the range from 1,53 to 1,58. The glass contains silicon dioxide  $\text{SiO}_2$ , aluminium oxide  $\text{Al}_2\text{O}_3$ , zirconium  
10        dioxide  $\text{ZrO}_2$ , calcium  $\text{CaO}$  and/or magnesium  $\text{MgO}$  oxide, potassium  $\text{K}_2\text{O}$  and/or sodium  $\text{Na}_2\text{O}$  oxide.

### Background art

15        The classification of crystal utility glass types according to ČSN 70 001 is as follows:

- crystal soda potash glass containing in total potassium  $\text{K}_2\text{O}$  and sodium  $\text{Na}_2\text{O}$  oxides  $\geq 10\%$  by weight, the value of refractive index being not required
- crystal glass containing potassium  $\text{K}_2\text{O}$ , barium  $\text{BaO}$   
20        and lead oxides in total  $\geq 10\%$  by weight, with the refractive index of about 1,51
- special crystal glass containing potassium oxide  $\text{K}_2\text{O}$ , zirconium dioxide  $\text{ZrO}_2$ , barium  $\text{BaO}$  and lead oxides in total  $\geq 10\%$  by weight, with the refractive index  
25        from 1,51 to 1,525
- lead crystal glass with the content of lead oxide  $\geq 24\%$  by weight with the refractive index of  $\geq 1,545$
- high lead crystal glass with the content of lead oxide  $\geq 30\%$  by weight with the refractive  
30        index  $\gg 1,545$ .

Also, the crystal soda potash glass which is a czech speciality from the historical point of view. Remaining crystal glass types correspond to EC - directions. The first two crystal glass types mentioned above are being  
35        used for products from so called cheap crystal glass which are accented above all by a low price and refractive index ranges about the value of 1,51.

- 2 -

Barium BaO and lead oxides being used by some manufacturers and in smaller amounts only, as is stated e.g. by A. Smrček in the journal Sklář a keramik 38, /1988/, p. 286-294. The group of specialty crystal glass types represents more noble products in which the refractive index is observed to range about the value 1,52 and which is obtained by dosing of barium BaO and zinc ZnO oxides, alternatively also of lead oxide, as is specified e.g. in BRD-patent from 1987 No. 2839645, such a glass according to the said patent contains in % by weight as follows: silicon dioxide  $\text{SiO}_2$  65 to 75, aluminium oxide  $\text{Al}_2\text{O}_3$  0,1 to 2, calcium oxide CaO 2 to 12, magnesium oxide MgO 0 to 8, sodium oxide  $\text{Na}_2\text{O}$  7 to 15, potassium oxide  $\text{K}_2\text{O}$  0 to 10, lithium oxide  $\text{Li}_2\text{O}$  0 to 3, barium oxide BaO 1 to 6, zinc oxide ZnO 0,2 to 3, lead oxide 0 to 10 and titanium dioxide  $\text{TiO}_2$  0,2 to 5. This invention covers by its chemical composition, with the exception of titanium dioxide  $\text{TiO}_2$ , most of crystal glass types being produced excepting of lead and high-lead crystal glass types with the content of lead oxide  $\geq 24$  % by weight.

For the products of luxurious character which are decorated predominately by grinding the lead and high-lead crystal glass types are being used where the refractive index of  $\geq 1,545$  is required. At the present time the unharmed hygienic properties are being preferred particularly concerning the content of lead and barium in the leach. With regard to a fact that in the production of those special crystal glass types the refractive index of the desired value is being elevated largely by an increased amount of barium BaO and lead oxides, the said hygiene properties that are required induce insolvable problems in the production of such glass types.

#### Disclosure of the invention

According to this invention the disadvantages

- 3 -

mentioned above are removed or substantially reduced by using the crystal lead-free glass with the content of zirconium dioxide  $ZrO_2$  which is characterized by the content from 50 to 65 % by weight of silicon dioxide  $SiO_2$ , from 0,1 to 10 % by weight of aluminium oxide  $Al_2O_3$ , from 0,5 to 17 % by weight of zirconium dioxide  $ZrO_2$ , from 10 to 22 % by weight of potassium  $K_2O$  and/or sodium  $Na_2O$  oxide, from 2 to 10 % by weight of calcium  $CaO$  and/or magnesium  $MgO$  oxide, the total amount of iron  $Fe$  expressed as iron trioxide  $Fe_2O_3$  (ferric oxide) being ranged from 0,01 to 0,025 % by weight.

The functional and technological properties are with advantage modified by using at least one oxide from the group containing barium  $BaO$ , zinc  $ZnO$ , boron  $B_2O_3$  and lithium  $Li_2O$  oxides amounted from 0,1 to 10 % by weight of barium  $BaO$ , zinc  $ZnO$ , boron  $B_2O_3$  and lithium  $Li_2O$  oxides.

This glass type can with advantage contain traces to 1 % by weight of antimony trioxide  $Sb_2O_3$ , titanium dioxide  $TiO_2$  and stannic dioxide  $SnO_2$  either separately or in combination as further modifiers.

The advantage of said glass type is the decorative cutting and engraving ability comparable with the lead crystal glass, while having no content of lead oxide which is unhealthy and environmentally harmful. During melting of said glass type there does not occur the volatilization of environmentally harmful lead oxides and arsenic that are used in the manufacture of lead crystal glass. Thus, as the lead-free glass type is preferred which is intended especially for the utility glass, i.e. also for beverage packing glass and domestic glass, it features the advantage of undesirable and unhealthy lead oxide being not penetrated into the leach. The melting and refining of said molten glass types is easier when compared with lead crystal molten glass types as the lead-free glass types feature lower melting temperatures.

Especially, the melting temperature and the

- 4 -

temperature point of liquidus are improved by addition of modifying additives, namely of barium BaO, zinc ZnO, boron B<sub>2</sub>O<sub>3</sub> and lithium Li<sub>2</sub>O oxides. Moreover, said oxides positively affect the refractive index of glass.

- 5       The antimony trioxide Sb<sub>2</sub>O<sub>3</sub> is used for the refining ability to be improved. Both titanium dioxide TiO<sub>2</sub> and stannic oxide SnO including antimony trioxide Sb<sub>2</sub>O<sub>3</sub> also increase the value of the refractive index.

- 5 -

Examples of carrying out invention

The invention will be further described, by way of the following examples of carrying out.

5	Example No.	1	2	3	4
	Glass component	content in % by weight			
	Silicium dioxide $\text{SiO}_2$	60,68	58,31	61,75	60,77
	Aluminium oxide $\text{Al}_2\text{O}_3$	5,00	0,38	5,00	5,00
10	Zirconium dioxide $\text{ZrO}_2$	8,3	14,9	3,5	3,5
	Calcium oxide $\text{CaO}$	6,00	5,58	5,40	5,40
	Magnesium oxide $\text{MgO}$	0,00	0,40	0,00	0,00
	Sodium oxide $\text{Na}_2\text{O}$	12,00	19,87	7,00	8,00
	Potassium oxide $\text{K}_2\text{O}$	8,00	0,25	6,00	6,00
15	Barium oxide $\text{BaO}$	0,00	0,00	9,00	0,00
	Zinc oxide $\text{ZnO}$	0,00	0,00	0,00	9,00
	Lithium oxide $\text{Li}_2\text{O}$	0,00	0,00	0,00	2,00
	Antimony trioxide $\text{Sb}_2\text{O}_3$	0,00	0,29	0,33	0,32
	Iron content expressed by amount of				
20	iron trioxide	0,015	0,02	0,02	0,01
	Total oxides	100,00	100,00	100,00	100,00
	$t_{\log \eta=2}$ [°C]	1504	1405	1430	1408
	$t_{\log \eta=4}$ [°C]	1114	1087	1012	1008
25	$t_{\log \eta=7,65}$ [°C]	827	844	714	721
	$t_{\log \eta=13}$ [°C]	637	678	523	535
	$t_{\log \eta=14,5}$ [°C]	602	647	489	501
	$t_{\text{liquidus}}$ [°C]	963	1210	930	950
	refractive index				
30	at 589,3 [nm]	1,545	1,572	1,542	1,543
	density at 20 °C [ $\text{g.cm}^{-3}$ ]	2,628	2,754	2,685	2,683
	$\alpha_{20-300^\circ\text{C}} \cdot 10^6$ [°C $^{-1}$ ]	9,16	9,37	8,80	8,82
	grindability [ $\mu\text{m.min}^{-1}$ ]				
35		0,312	0,343	0,329	0,372

- 6 -

E x a m p l e N o. Glass components		5	6	7
		content in % by weight		
5	Silicium dioxide $\text{SiO}_2$	60,37	60,17	66,07
	Aluminium oxide $\text{Al}_2\text{O}_3$	7,00	5,00	0,00
	Zirconium dioxide $\text{ZrO}_2$	6,30	8,30	5,00
	Calcium oxide $\text{CaO}$	6,00	6,00	5,40
	Sodium oxide $\text{Na}_2\text{O}$	10,00	10,00	6,00
10	Potassium oxide $\text{K}_2\text{O}$	8,00	8,00	6,00
	Lithium oxide $\text{Li}_2\text{O}$	2,00	0,00	2,00
	Barium oxide $\text{BaO}$	0,00	0,00	6,00
	Zinc oxide $\text{ZnO}$	0,00	0,00	3,00
	Boron oxide $\text{B}_2\text{O}_3$	0,00	2,00	0,00
15	Antimony trioxide $\text{Sb}_2\text{O}_3$	0,31	0,32	0,31
	Titanium dioxide $\text{TiO}_2$	0,00	0,20	0,00
	Stannic dioxide $\text{SnO}_2$	0,00	0,00	0,20
Iron content expressed by amount of iron trioxide		0,02	0,01	0,02
20	Total oxides	100,00	100,00	100,00
	$t_{\log \eta=2}$ [°C]	1425	1518	1470
	$t_{\log \eta=4}$ [°C]	1027	1112	1040
	$t_{\log \eta=7,65}$ [°C]	739	815	738
	$t_{\log \eta=13}$ [°C]	552	621	539
	$t_{\log \eta=14,5}$ [°C]	518	556	503
	$t_{\text{liquidus}}$ [°C]	970	950	844
	refractive index at 589,3 [nm]	1,543	1,545	1,544
	density at 20 °C [ $\text{g.cm}^{-3}$ ]	2,5909	2,6206	2,6748
	$\alpha_{20-300^\circ\text{C}} \cdot 10^6$ [°C $^{-1}$ ]	8,90	7,93	8,68
30	grindability [ $\mu\text{m.min}^{-1}$ ]	0,279	0,192	0,185



- 7 -

In the presented examples corresponds  $t_{\log \eta=2}$  to the temperature of glass melting,  $t_{\log \eta=4}$  to the temperature of glass forming,  $t_{\log \eta=7.65}$  to the temperature of Littleton point of glass softening,  $t_{\log \eta=13}$  to the upper annealing temperature and  $t_{\log \eta=14.5}$  to the lower annealing temperature and  $\alpha_{20-300^{\circ}\text{C}}$  to the mean coefficient of thermal expansivity of glass in the range from 20 to 300 °C. The grindability is expressed by a loss of sample weight in  $\mu\text{m} \cdot \text{min}^{-1}$  onto a diamond grinding wheel with the dimensions of grain 120  $\mu\text{m}$  under loading of 1,71  $\text{g} \cdot \text{mm}^{-2}$ .

The melting temperature that corresponds to the molten glass viscosity of  $\log \eta = 2$  is approximately 1500 °C for the lead glass types. For glass types according to this invention is either comparable with lead glass types or e.g. in accordance with the examples No. 1 and No. 6 or lowered by 30 °C for the molten glass type according to the example No. 7, by 75 °C for the molten glass according to the example No. 5, by 92 °C for the molten glass according to the example No. 4, by 70 °C for the molten glass according to the example No. 3 and by 95 °C for the molten glass according to the example No. 2.

All temperatures of point of liquidus except of the composition No. 2 that is characterized by a high content of zirconium dioxide, are lower than the forming temperatures corresponding to the temperature at a viscosity of molten glass  $\log \eta = 4$  so that with these molten glass types the tendency to undesirable crystallization is restrained.

For the lead crystal the refractive index is approximately 1,545, for the glass types according to this invention it ranges within 1,542 and 1,572. Thus, the optical properties of final products are comparable or better ones when comparing with products made of lead crystal glass which will especially reflect on decorative cut and engraved products.

- 8 -

5 The mean coefficient of linear thermal expansivity  $\alpha$  within range from 20 to 300 °C is in all cases lower than for so far used crystal glass types in general which is favourable for the resistance of glass against the thermal shock.

10 The grindability for the lead crystal glass is according to the chosen method 0,266  $\mu\text{m}.\text{min}^{-1}$  and for embodiments according to the composition No. 1 to No. 5 it is higher which will favourable affect the velocity of processing of these glass types by means of decorative cutting and engraving.

#### Industrial applicability

15 The lead-free crystal glass according to this invention with the content of zirconium dioxide  $\text{ZrO}_2$  is intended for man-made and machine-made utility glassware with a higher refractive index, it is suitable particularly for glass decorated by cutting and engraving and by further decorative techniques for products of the  
20 luxurious character. This glass type is hygienic unharmed concerning the content of detrimental substances in the leach and by its brilliance can compete with the products made of lead crystal glass.

25 The question there is both the production of glass objects used in households and restaurants, e.g. small cups, tumblers, carafes, bowls and vessels of various shapes and sizes used for decorative purposes, such as vases, dishes etc.

- 9 -

Claims

1. Crystal lead-free glass suitable especially for  
5 man-made and machine-made utility glass with the  
refractive index within the range from 1,53 to 1,58,  
containing silicon dioxide  $\text{SiO}_2$ , aluminium oxide  
 $\text{Al}_2\text{O}_3$ , zirconium dioxide  $\text{ZrO}_2$ , calcium  $\text{CaO}$  and/or  
magnesium  $\text{MgO}$  oxide, potassium  $\text{K}_2\text{O}$  and or sodium  
10  $\text{Na}_2\text{O}$  oxide, characterized by its composition, with  
the content of 50 to 65 % by weight of silicon  
dioxide  $\text{SiO}_2$ , 0.1 to 10 % by weight of aluminium  
oxide  $\text{Al}_2\text{O}_3$ , 0.5 to 17 % by weight of zirconium  
dioxide  $\text{ZrO}_2$ , 10 to 22 % by weight of potassium  $\text{K}_2\text{O}$   
15 and/or sodium  $\text{Na}_2\text{O}$  oxide, 2 to 10 % by weight of  
calcium  $\text{CaO}$  and/or magnesium  $\text{MgO}$  oxide, the content  
of ferric oxide  $\text{Fe}_2\text{O}_3$  being within the range from 0,01  
to 0,025 % by weight.
- 20 2. Crystal lead-free glass according to claim 1,  
characterized by its composition, with the range from  
0,1 to 10 % by weight of barium oxide  $\text{BaO}$ , zinc oxide  
 $\text{ZnO}$ , boron trioxide  $\text{B}_2\text{O}_3$  and lithium oxide  $\text{Li}_2\text{O}$ .
- 25 3. Crystal lead-free glass according to claims 1 and  
2, characterized by its composition, with the  
content, individually or in a combination, of the  
traces to 1% by weight of antimony trioxide  $\text{Sb}_2\text{O}_3$ ,  
titanium dioxide  $\text{TiO}_2$  and stannic dioxide  $\text{SnO}_2$ .

30

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/CS 92/00012

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C03C3/087; C03C3/093		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C03C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	CHEMICAL ABSTRACTS, vol. 109, no. 16, 9 October 1988, Columbus, Ohio, US; abstract no. 133790Y, page 292 ; see abstract & JP,A,63 147 843 (NIPPON SHEET GLASS CO) 20 June 1988	1-3
Y	EP,A,0 405 579 (KIRIN BEER K.K.) 2 January 1991 see page 3, line 24 - page 5, line 14	1-3
Y	US,A,4 065 317 (BAAK) 27 December 1977 see column 3, line 19 - line 32; claims see column 11, line 26 - line 31	1-3
	--- -/--	
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15 JULY 1992	21. 07. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	VAN BOMMEL L.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	
Y	CHEMICAL ABSTRACTS, vol. 85, no. 8, 23 August 1976, Columbus, Ohio, US; abstract no. 50963S, page 282 ; see abstract & JP,A,51 055 310 (SUWA SEIKOSHA CO.) 15 May 1976 ---	1-3
Y	CHEMICAL ABSTRACTS, vol. 106, no. 18, 4 May 1987, Columbus, Ohio, US; abstract no. 142815A, page 287 ; see abstract & JP,A,61 270 234 (TOSHIBA GLASS CO.) 29 November 1986 ---	1-3
Y	WORLD PATENTS INDEX Week 7242, Derwent Publications Ltd., London, GB; AN 72-67211T & SU,A,330 119 (VLADIMIR POLYTECHNIC) 24 February 1972 see abstract ---	1-3

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

CS 9200012  
SA 58812

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 15/07/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A-63147843	20-06-88	None	
EP-A-0405579	02-01-91	JP-A- 3037131	18-02-91
US-A-4065317	27-12-77	None	
JP-A-51055310	15-05-76	None	
JP-A-61270234	29-11-86	None	